Available online at www.sciencedirect.com
ScienceDirect
Vibrational Spectroscopy 43 (2007) 380–386
VIBRATIONAL SPECTROSCOPY
www.elsevier.com/locate/vibspec

# Cooperative hydrogen bonding in solution: Influence of molecule structure

B.N. Solomonov *, M.A. Varfolomeev, D.I. Abaidullina

*Chemical Institute, Kazan State University, Kremlevskaya 18, Kazan 420008, Russia*

Received 3 March 2006; received in revised form 14 April 2006; accepted 20 April 2006
Available online 12 June 2006

**Abstract**

Influence of cooperative interactions on IR stretching vibration frequencies of complexes $CCl_3H\cdots ROH\cdots B$ (B-base), $CCl_3H\cdots ROH\cdots O(C_2H_5)_2$ and $CCl_3H\cdots ROH\cdots ROH$ in proton donor solvent $CCl_3H$ were studied.

Solvent effects on OH stretching vibration frequencies of $CF_3CH_2OH\cdots B$, $ROH\cdots O(C_2H_5)_2$ and $ROH\cdots ROH$ complexes in aprotic solvents were calculated using earlier proposed method. Cooperativity factors in $CCl_3H\cdots CF_3CH_2OH\cdots B$ complexes were determined. Obtained values were significant smaller than for $CCl_3H\cdots CH_3OH\cdots B$ complexes. Also cooperativity factors for $CCl_3H\cdots ROH\cdots O(C_2H_5)_2$ and $CCl_3H\cdots ROH\cdots ROH$ complexes were determined. It was demonstrated that obtained values slightly depend on length and embranchment of alkyl group in alcohol molecules. The main role in cooperative interactions plays electronic effect.

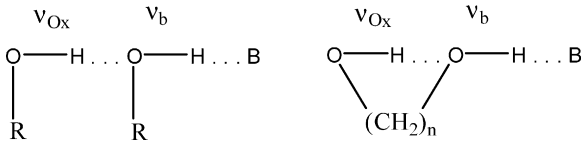

*Keywords:* Cooperativity; Hydrogen bonding; Solvent effect; FT-IR spectroscopy

## 1. Introduction

Hydrogen bonding (HB) plays a great role in different regions of chemistry [1]. One of the particular properties of HB is cooperativity. Concept of cooperativity between HB implies that the primary H-bond formed between proton donor X–H and proton acceptor B, X–H···B, becomes stronger when a third partner, Y–H, forms another hydrogen bonding with a lone pair of atom X (Y–H···X–H···B) [2–6].

Hydrogen bonding cooperativity is investigated by IR- and NMR-spectroscopy methods in solution [7–16], in solid state [17], including argon matrix [18–21]. The cooperativity phenomenon is being extensively studied with an accent on theoretical investigations [22–44].

The works on quantitative investigation of cooperative hydrogen bonds were made by Kleeberg and coworkers using IR spectroscopy method [12–15]. Authors have evaluated cooperativity factors $A_b$ and $A_{Ox}$ for complexes:




For these systems $\nu_{Ox}$ and $\nu_b$ frequencies were obtained in proton acceptor environment or inert solvent. Cooperativity factors are defined as slopes of linear correlation between experimental frequencies $\nu_{Ox}$ and $\nu_b$ and the frequency of O–H band in ROH···B complexes, respectively. Later it was shown that method of determination of cooperativity factors proposed by Kleeberg and coworkers [12–15] have some imprecision's.

Recently, in Ref. [45] a new method for determining cooperativity factors in complexes ROH···ROH···B were proposed. It was found that H-bonds in these complexes are strengthened. Cooperativity factor $A_{Ox}$ for ROH···ROH···B system increases and cooperativity factor $A_b$ decreases with increasing the acceptor strength of B. The obtained results are in good agreement with the data obtained previously from matrix-isolation FT-IR spectroscopy in solid argon [18].

Influence of cooperative interactions on stretching vibration frequencies of complexes Y–H···X–H···B or Y–H···X–

* Corresponding author. Tel.: +7 8432 315343; fax: +7 8432 315346.
*E-mail address:* Boris.Solomonov@ksu.ru (B.N. Solomonov).

0924-2031/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.vibspec.2006.04.024